Customized FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY DOCKET NO.
P07223US00/LRP

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
09/856358

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP99/06502	22 November 1999	24 November 1998

TITLE OF INVENTION: ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

APPLICANT(S) FOR DO/EO/US: KEZUKA ET AL.

Applicant herewith submits to the US Designated/Elected Office (DO/EO/US) the following items and other information:

X 1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 USC 371.

X 3. This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 USC 371(b) and PCT Art. 22 and 39(1).

X 4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. A **copy** of the International Application as filed (35 U.S.C. 371 (c)(2))
   - a. is transmitted herewith (required only if not transmitted by the International Bureau).
   - X b. has been transmitted by the International Bureau.
   - c. is not required, as the application was filed in the United States Receiving Office (RO/US).

X 6. A **translation** of the International Application into English (35 U.S.C. 371(c)(2)).

7. Amendments to the claims of the International Appln. under PCT Article 19 (35 USC 371 (c)(3))
   - a. are transmitted herewith (required only if not transmitted by the International Bureau).
   - b. have been transmitted by the International Bureau.
   - c. have not been made; however, the time limit for making such amendments had NOT expired.
   - d. have not been made and will not be made.

8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

X 9. An **oath** or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. A translation of the annexes to the Int'l Prelim. Exam. Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. An **Information Disclosure Statement** under 37 C.F.R. 1.97 and 1.98.

X 12. An **Assignment** document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

X 13. A **First preliminary amendment**.

14. A Second or Subsequent preliminary amendment.

15. A substitute specification.

X 16. A change of power of attorney and/or address letter.

17. A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 & 35 USC 1.821-825.

18. A second copy of the published international application under 35 USC 154(d)(4).

19. A second copy of the English translation of the international application under 35 USC 154(d)(4).

20. Other items or information:

A copy of the Notification of Missing Requirements under 35 U.S.C. 371.

X In the event that a petition for extension of time is required to be submitted herewith, and in the event that a separate petition does not accompany this response, applicant hereby petitions under 37 CFR 1.136(a) for an extension of time of as many months as are required to render this submission timely. Any fee is authorized in 17(c).

Date: May 22, 2001

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JC18 Rec'd PCT/PTO 22 MAY 2001

U.S. APPLICATION NO. (If known) 09/856358	INTERNATIONAL APPLICATION NO. PCT/JP99/06502	ATTORNEY DOCKET NO. P07223US00/LRP

		CALCULATIONS *PTO USE ONLY*
X	21. **The following fees are submitted:**	
X	**Basic National Fee** (37 CFR 1.492 (a) (1)-(5):	
	Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO $1000	
X	Search Report has been prepared by the EPO or JPO $ 860	
	No Int'l Prelim. Ex. fee paid to USPTO but Int'l Search fee paid to USPTO $ 710	
	International preliminary examination fee paid to USPTPO $ 690	
	Int'l Prelim. Ex. fee paid to USPTO & all claims satisfied PCT Art. 33(1)-(4) $ 100	
	ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860
	Surcharge of $130 for furnishing the oath or declaration later than [ ] 20 mos. [ ] 30 mos. + from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0

CLAIMS	*NUMBER FILED*	*NUMBER EXTRA*	*RATE*	
Total Claims	16 - 20 =	0	X **$18** =	$ 0
Independent Claims	1 - 03 =	0	X **$80** =	$ 0
Multiple Dependent Claim(s) (if applicable)			+ **$270** =	$ 0
			TOTAL OF ABOVE CALCULATIONS =	**$ 860**
	Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½.		-	$
			SUBTOTAL =	**$ 860**
	Processing fee of **$130** for furnishing the **English translation** later than [ ] 20 mos. [ ] 30 mos. + from the earliest claimed priority date (37 CFR 1.492(f)).			$ 0
			TOTAL NATIONAL FEE =	**$ 860**
X	Fee for recording the enclosed **assignment** (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40** per property		+	$ 40
			TOTAL FEES ENCLOSED =	**$ 900**
			Amount to be *Refunded*	*$*
			Charged	*$*

X	a. A **check** in the amount of $900.00 to cover the above fees is enclosed.
	b. Please charge my Deposit Account No. 12-0555 in the amount of $ to cover the above fees.
X	c. The Commissioner is hereby authorized to charge any additional fees required or credit overpayment to Deposit Account No. 12-0555.

Note: *Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.*

SEND ALL CORRESPONDENCE TO:

Linda R. Poteate

At the address (below) of **CUSTOMER NO. 000881.**

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REG. NO.: 28,518

PHONE NO.: 703-739-4900

Date: May 22, 2001

Customized FORM PTO-1390

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent

In re patent application of: KEZUKA ET AL.

Serial No.: Unassigned

Examiner: Unassigned

Filed: May 22, 2001

Art Unit: Unassigned

For: ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

Docket No.: P07223US00/LRP

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents

Washington, D.C. 20231

SIR:

Prior to examination, please amend the above-identified application as follows:

IN THE CLAIMS

A clean version of all amended claim 14 is provided herewith in **Attachment A**. It will be noted that claim 14 has been amended relative to the previously provided version submitted with the application shown by the marked up version thereof in **Attachment B** provided herewith.

REMARKS

The present Amendment is made to eliminate multiple dependency in the claims.

Respectfully submitted,

Date: May 22, 2001

By: Douglas E. Jackson Jr.
Registration No.: 28,518

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ATTACHMENT A

Clean Replacement/New Claims

Following herewith is a marked up copy of each rewritten claim.

15. (AMENDED) A method for producing an etched article by etching an article to be etched with the etching solution as defined in claim 1.

ATTACHMENT B

Marked Up Replacement Claims

Following herewith is a marked up copy of each rewritten claim.

15. (AMENDED) A method for producing an etched article by etching an article to be etched with the etching solution as defined in ~~any of claims 1-14~~ claim 1.

DESCRIPTION

ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

TECHNICAL FIELD

The present invention relates to an etching solution, a method for producing an etched article and an etched article produced by the method, more specifically, an etching solution and a method for producing an etched article for selectively etching a doped oxide film, particularly BSG or BPSG relative to an undoped oxide film, particularly THOX, and an etched article produced by the method.

BACKGROUND ART

Conventionally, as etchants for silicon wafers and the like have been used buffered hydrofluoric acids comprising HF (50% by weight) and NH_4F (40% by weight) at such a ratio that can achieve a desired etch rate.

However, the buffered hydrofluoric acids etch not only doped oxide films such as BSG films, BPSG films, phosphosilicate glass (PSG) films, arsenic silicate glass (AsSG) films and the like, but also undoped oxide films such as USG including TEOS (oxide obtained by CVD method using tetraethoxysilane gas) films, THOX and the like. Therefore, the buffered hydrofluoric acids can not selectively etch the doped oxide films.

An object of the present invention is to provide an etching solution and an etching method for selectively etching oxide films doped with impurities relative to TEOS and THOX.

DISCLOSURE OF INVENTION

The present invention relates to the items 1-16 listed below.

Item 1: An etching solution comprising hydrofluoric acid, wherein an a ratio of etch rate of a boron silicate glass film (BSG) or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher.

Item 2: The etching solution according to item 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.

Item 3: The etching solution according to item 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

Item 4: The etching solution according to item 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.

Item 5: The etching solution according to item 1,

wherein the weight ratio of HF : isopropyl alcohol : water is 0.1-50% by weight : 30-99% by weight : 0-70% by weight.

Item 6: The etching solution according to item 1, wherein the weight ratio of HF : acetic acid : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

Item 7: The etching solution according to item 1, wherein the weight ratio of HF : tetrahydrofuran : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

Item 8: The etching solution according to item 1, wherein the weight ratio of HF : acetone : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

Item 9: The etching solution according to item 1, wherein the weight ratio of HF : methanol : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

Item 10: The etching solution according to item 1, wherein the weight ratio of HF : ethanol : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

Item 11: The etching solution according to item 1, the solution comprising an inorganic acid.

Item: 12 The etching solution according to item 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower.

Item 13: The etching solution according to item 11,

wherein the weight ratio of HF : HCl : water is 0.01-50% by weight : 1-36% by weight : 0-99% by weight.

Item 14: The etching solution according to item 11, wherein the weight ratio of HF : HNO_3 : water is 0.01-50% by weight : 1-70% by weight : 0-99% by weight.

Item 15: A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of items 1-14.

Item 16: An etched article which is obtainable by the method of item 15.

According to the etching solution of the invention, the ratio of BSG etch rate / THOX etch rate and/or the ratio of BPSG etch rate / THOX etch rate at 25°C is/are 10 or higher, preferably 20 or higher, more preferably 50 or higher, particularly 100 or higher.

In case of using TEOS instead of THOX, the ratio of BSG etch rate / TEOS etch rate and/or the ratio of BPSG etch rate / TEOS etch rate at 25°C is/are 5 or higher, preferably 10 or higher, more preferably 50 or higher, particularly 100 or higher.

The etch rate of the etching solution of the invention can be calculated as the difference in thickness of a film (BSG; BPSG; THOX; TEOS and like USG, etc.) before and after etching divided by etch time.

The water content is not higher than 70% by

weight, preferably not higher than 30% by weight, more preferably about 30-5% by weight. The relative dielectric constant of the etching solution expresses an arithmetic mean of the relative dielectric constants of the components of the etching solutions other than the HF and inorganic acid.

Preferable examples of the inorganic acid include inorganic acids having a pKa value at 25°C of 2 or lower, for example, hydrochloric acid (pKa =-8), nitric acid (pKa=-1.8), hydrobromic acid (pKa=-9), hydroiodic acid (pKa=-10) and perchloric acid (a pKa-unmeasurably strong acid).

Examples of the organic acid include acetic acid (relative dielectric constant: 6.15 (20°C)), propionic acid (relative dielectric constant: 3.4 (40°C)), butyric acid (relative dielectric constant: 2.97(20°C)), isobutyric acid (relative dielectric constant: 2.73(40°C)), valeric acid, caproic acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative dielectric constant: 2.45(20°C)), monochloroacetic acid (relative dielectric constant: 21 (20°C)), dichloroacetic acid (relative dielectric constant: 8.08(20°C)), trichloroacetic acid (relative dielectric constant: 4.6 (60°C)), monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, α-chlorobutyric acid, β-

chlorobutyric acid, γ-chlorobutyric acid, lactic acid (relative dielectric constant: 22(70°C)), glycolic acid, pyruvic acid, glyoxalic acid, acrylic acid and like monocarboxylic acids, methanesulfonic acid, toluenesulfonic acid and like sulfonic acids, oxalic acid, succinic acid, adipic acid, tartaric acid, citric acid and like polycarboxylic acids.

Examples of the organic solvent having a hetero atom include methanol (relative dielectric constant: 32.6 (25°C)), ethanol (relative dielectric constant: 24.6 (25°C)), isopropanol (IPA, relative dielectric constant: 19.9 (25°C)), 1-propanol (relative dielectric constant: 22.2 (25°C)), 1-butanol (relative dielectric constant: 17.1 (25°C)), 2-butanol (relative dielectric constant: 15.5 (19°C)), t-butanol (relative dielectric constant: 11.4 (19°C)), 2-methyl-1-propanol (relative dielectric constant: 17.95 (20°C)), 1-pentanol (relative dielectric constant: 13.9 (25°C)), 1-hexanol (relative dielectric constant: 13.3 (25°C)), 1-heptanol, 4-heptanol, 1-octanol (relative dielectric constant: 10.34 (20°C)), 1-nonylalcohol, 1-decanol, 1-dodecanol and like alcohols; ethylene glycol (relative dielectric constant: 37.7 (20°C)), 1,2-propanediol (relative dielectric constant: 32.0 (20°C)), 2,3-butanediol, glycerin (relative dielectric constant: 42.5 (25°C)) and like polyols,

acetone (relative dielectric constant: 20.7 (25°C)), acetylacetone, methyl ethyl ketone (relative dielectric constant: 18.51 (20°C)) and like ketones; acetonitrile (relative dielectric constant: 37.5 (20°C)), propionitrile (relative dielectric constant: 29.7 (20°C)), butyronitrile (relative dielectric constant: 20.3 (20°C)), isobutyronitrile (relative dielectric constant: 20.4 (20°C)), benzonitrile (relative dielectric constant: 25.2 (25°C)) and like nitriles; formaldehyde, acetaldehyde, propionaldehyde and like aldehydes; ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and like alkylene glycol mono alkyl ethers; tetrahydrofuran (relative dielectric constant: 7.6 (25°C)), dioxane (relative dielectric constant: 2.2 (25°C)) and like ethers, trifluoroethanol, pentafluoropropanol, 2,2,3,3-tetrafluoro propanol and like fluorine alcohols, sulfolane (relative dielectric constant: 43.3 (20°C)), nitromethane (relative dielectric constant: 35.87 (30°C)) and the like.

The relative dielectric constant of water is 78.3 (25°C).

The content of HF is about 0.01-50% by weight, preferably about 1-5% by weight.

The water content is not higher than 70% by weight, preferably not higher than 30% by weight, more

preferably about 0-5% by weight.

The content of the inorganic acid is about 1-99% by weight, preferably about 30-70% by weight.

The content of the organic acid is about 30-99.9% by weight, preferably about 70-99.9% by weight.

The content of the organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

The content of at least one member selected from the group consisting of the inorganic acid, organic acid and organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

The inorganic acid has a pKa at 25°C of about 2 or lower, preferably about -5 or lower.

The relative dielectric constant of the organic acid and organic solvent having an hetero atom is preferably about 40 or lower, more preferably about 10 or lower.

As the HF is usually used dilute hydrofluoric acid (50 wt. % aqueous solution). However, when the HF does not contain water, 100% HF may be also used.

In case of HCl, HBr and HI, an anhydrous etching solution can be prepared by blowing these gases through the etching solution.

Preferable etching solutions of the present

invention and their compositions are shown below.

·HF: IPA : water = 1-10% by weight : 70-99% by weight : 0-30% by weight

·HF: acetic acid : water = 0.5-5% by weight : 70-99.5% by weight : 0-30% by weight

·HF : HCl : water = 0.01-5% by weight : 1-36% by weight : 50-99% by weight

·HF : nitric acid : water = 0.01-5% by weight : 1-70% by weight : 20-99% by weight

·HF: acetone : water = 1-10% by weight : 70-99% by weight : 0-30% by weight

·HF: THF : water = 1-10% by weight : 70-99% by weight : 0-30% by weight

·HF: methanol : water = 1-10% by weight : 70-99% by weight : 0-30% by weight

·HF: ethanol : water = 1-10% by weight : 70-99% by weight : 0-30% by weight

The etching solution of the invention can be suitably used for selectively etching a doped oxide film of an article to be etched comprising an oxide film (BSG, BPSG, etc.) doped with B, P and the like and an undoped oxide film such as THOX, TEOS and like.

In the etching method of the present invention, the temperature of the etching solution is about 15-40°C.

Examples of the article to be etched include

single crystalline silicon wafers, gallium-arsenic wafers and like wafers, especially the articles comprising a doped oxide film (BSG, BPSG, etc.) and an undoped oxide film (THOX, TEOS and like USGs).

The BSG etch rate of the etching solution of the invention is usually about 10-2000 nm/min, preferably about 40-500 nm/min.

The present invention can provide an etching solution which can selectively etch films doped with impurities, such as BSG, BPSG and the like, relative to THOX, TEOS and like USG, a method for producing an etched article using the etching solution and an etched article.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be explained in more detail with referring to Examples and Comparative Examples below.

Examples 1-2 and Comparative Examples 1-4 (inorganic acid)

Etching solutions were prepared by mixing HF, water, an organic solvent having a hetero atom (isopropyl alcohol (IPA), THF, acetone, methanol, ethanol), an organic acid (acetic acid) and inorganic acid (HCl, HNO_3) in the ratios shown in Table 1. Test substrates were produced by forming each of a thermal oxide (THOX) film, USG (TEOS) film, boron silicate glass (BSG) film and

boron phosphosilicate glass (BPSG) film on a silicon substrate by CVD method using a tetraethoxysilane gas. The etch rate and etch selectivity of the etching solutions on the test substrates were determined.

In addition, the etch rate and selectivity of conventional $HF-H_2O$ and $HF-NH_4F-H_2O$ etching solutions were determined in the above-mentioned manner as Comparative Examples.

The etch rate was determined by measuring the thickness of the films before and after etching with an Auto EL-III ellipsometer manufactured by Rudolf Research.

The etch rates of the etching solutions were calculated as the difference in thickness of films before and after being etched at 25°C divided by etch time.

The results of the etching solutions with each composition are shown in Table 1 to Table 8.

The relative dielectric constant is that of a solvent (an organic solvent having a hetero atom or an organic acid) + water at 25°C, expressed as a calculated value of an average of the relative dielectric constants of the solvent and water having the particular composition.

Average of relative dielectric constants = [78.3 x (percentage by weight of water) + (relative dielectric constant of solvent at 25°C) x (percentage by

weight of solvent)] / [(percentage by weight of water) + (percentage by weight of solvent)]

HF-H_2O-isopropyl alcohol (PA) etchant

	Solvent	Relative dielectric constant of solvent	HF concentration (%)	Water concentration (%)	Solvent (IPA) concentration (%)	Relative dielectric constant of solvent (IPA)+water (calculated value)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Ex. 1	IPA	19.9	5	5	90	23.0	12	11	370	330	31	28	34	30
Ex. 2	IPA	19.9	5	25	70	35.3	55	76	920	1160	17	21	12	15
Ex. 3	IPA	19.9	5	45	50	47.6	97	140	1190	1650	12	17	8.5	12
Ex. 4	IPA	19.9	5	65	30	59.9	140	200	1450	1950	10	14	7.3	9.8
Ex. 5	IPA	19.9	3	3	94	21.7	2	3	120	-	60	-	40	-
Ex. 6	IPA	19.9	10	10	80	26.4	59	82	2200	-	37	-	27	-
Ex. 7	IPA	19.9	15	15	70	30.2	350	230	6500	-	28	-	19	-
Ex. 8	IPA	19.9	20	20	60	34.5	820	1200	12000	-	15	-	10	-
Comp. Ex. 1	(Water)	(78.3)	1	99	0	-	58	93	380	-	6.5	-	4.1	-
Comp. Ex. 2	(Water)	(78.3)	2	98	0	-	120	190	750	-	6.3	-	3.9	-
Comp. Ex. 3	(Water)	(78.3)	3	95	0	-	300	490	1980	-	6.6	-	4.0	-

HF-H_2O-acetic acid etchant

	Solvent	Relative dielectric constant of solvent	HF concentration (%)	Water concentration (%)	Solvent (acetic acid) concentration (%)	Relative dielectric constant of solvent (acetic acid)+ water (calculated value)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Ex. 9	Acetic acid	6.15	1	1	98	6.88	10	14	530	750	53	75	38	54
Ex. 10	Acetic acid	6.15	1.25	1.25	97.5	7.06	12	18	1200	940	100	78	67	52
Ex. 11	Acetic acid	6.15	1.5	1.5	97	7.25	17	22	1600	1300	94	76	73	59
Ex. 12	Acetic acid	6.15	2	2	96	7.62	25	33	2600	-	100	-	79	-
Ex. 13	Acetic acid	6.15	2.5	2.5	95	8	32	45	3600	-	110	-	80	-
Ex. 14	Acetic acid	6.15	3	3	94	8.38	40	55	4600	-	120	-	84	-
Ex. 15	Acetic acid	6.15	5	5	90	9.95	97	140	8900	-	92	-	64	-
Ex. 16	Acetic acid	6.15	1.25	5	93.75	9.80	18	23	1600	-	89	-	70	-
Ex. 17	Acetic acid	6.15	1.25	10	88.75	13.5	20	32	1300	-	65	-	41	-
Ex. 18	Acetic acid	6.15	1.25	20	78.75	20.8	32	46	970	-	30	-	21	-
Ex. 19	Acetic acid	6.15	1.25	30	68.75	28.1	39	58	830	-	21	-	14	-
Ex. 20	Acetic acid	6.15	1.25	40	58.75	35.4	40	65	670	-	17	-	10	-
Ex. 21	Acetic acid	6.15	1.25	50	48.75	42.7	43	72	590	-	14	-	8.2	-

HF-H_2O-tetrahydrofurane (THF) etchant

	Sol-vent	Relative dielectric constant of solvent	HF con-cen-tra-tion (%)	Water con-cen-tra-tion (%)	Sol-vent (THF) con-cen-tra-tion (%)	Relative dielectric constant of solvent (THF)+water (calculated value)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Ex. 22	THF	7.6	5	5	90	11.3	3	4	510	330	170	110	130	83
Ex. 23	THF	7.6	5	25	70	26.2	31	42	690	830	22	27	16	20
Ex. 24	THF	7.6	5	45	50	41.1	64	85	890	1200	14	19	10	14
Ex. 25	THF	7.6	5	65	30	56.0	110	150	1200	1600	11	15	8	11

$HF-H_2O$-acetone etchant

	Solvent	Relative dielectric constant of solvent	HF concentration (%)	Water concentration (%)	Solvent (acetone) concentration (%)	Relative dielectric constant of solvent (acetone)+water (calculated value)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Ex. 26	Acetone	20.7	5	5	90	23.7	3	4	410	250	140	83	100	63
Ex. 27	Acetone	20.7	5	25	70	35.9	24	29	440	520	18	22	15	18
Ex. 28	Acetone	20.7	5	45	50	48.0	49	67	620	760	13	16	9.3	11
Ex. 29	Acetone	20.7	5	65	30	60.1	96	140	960	1300	10	14	6.9	9.3

HF-H_2O-methanol etchant

	Solvent	Relative dielectric constant of solvent	HF concentration (%)	Water concentration (%)	Solvent (methanol) concentration (%)	Relative dielectric constant of solvent (methanol)+water (calculated value)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Ex. 30	Methanol	32.6	3	3	94	34.0	0.5	7	44	73	88	150	6.3	10
Ex. 31	Methanol	32.6	5	5	90	35.0	3	9	170	230	57	77	19	26
Ex. 32	Methanol	32.6	10	10	80	39.9	22	43	730	410	33	19	17	9.5

$HF-H_2O$-ethanol etchant

	Solvent	Relative dielectric constant of solvent	HF concentration (%)	Water concentration (%)	Solvent (ethanol) concentration (%)	Relative dielectric constant of solvent (ethanol)+water (calculated value)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Ex. 33	Ethanol	24.6	5	5	90	27.4	7	9	250	210	36	30	28	23

$HF-NH_4F-H_2O$ etchant (Comparative Examples)

	Solvent	Relative dielectric constant of solvent	HF concentration (%)	NH_4F concentration (%)	Solvent (water) concentration (%)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Comp. Ex. 4	(Water)	(78.3)	1	39.1	59.9	170	230	110	-	0.6	-	0.5	-
Comp. Ex. 5	(Water)	(78.3)	2	2	96	280	480	620	-	2.2	-	1.3	-
Comp. Ex. 6	(Water)	(78.3)	2	5	93	320	640	440	-	1.4	-	0.7	-
Comp. Ex. 7	(Water)	(78.3)	2	10	88	400	700	350	-	0.9	-	0.5	-
Comp. Ex. 8	(Water)	(78.3)	2	20	78	420	720	270	-	0.6	-	0.4	-
Comp. Ex. 9	(Water)	(78.3)	2	30	68	390	610	230	-	0.6	-	0.4	-
Comp. Ex. 10	(Water)	(78.3)	2	38.7	59.3	300	450	200	-	0.7	-	0.4	-

HF-H_2O-acid-added etchant

	Added acid	pKa of acid	HF concentration (%)	Water concentration (%)	Acid concentration (%)	THOX etch rate (A/min.)	TEOS etch rate (A/min.)	BSG etch rate (A/min.)	BPSG etch rate (A/min.)	BSG/THOX selectivity	BPSG/THOX selectivity	BSG/TEOS selectivity	BPSG/TEOS selectivity
Ex. 34	HCl	-8	0.1	64	35.9	17	32	440	-	26	-	14	-
Ex. 35	HCl	-8	0.25	63.9	35.8	53	89	1200	-	23	-	13	-
Ex. 36	HCl	-8	0.5	63.9	35.6	120	200	2500	-	21	-	13	-
Ex. 37	HCl	-8	0.75	63.8	35.5	180	300	4300	-	24	-	14	-
Ex. 38	HCl	-8	1	63.7	35.3	240	380	4500	-	19	-	12	-
Ex. 39	HNO3	-1.8	1	30.4	68.6	240	340	5300	-	22	-	16	-
Comp. Ex. 11	H3PO4	2.15 (pKa1) 7.20 (pKa2) 12.4 (pKa3)	1	15.7	83.3	120	170	850	-	8.7 7.1	- -	5.9 5	- -

CLAIMS

1. An etching solution comprising hydrofluoric acid, wherein a ratio of an etch rate of a boron silicate glass film (BSG) or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher.

2. The etching solution according to claim 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.

3. The etching solution according to claim 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

4. The etching solution according to claim 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.

5. The etching solution according to claim 1, wherein the weight ratio of HF : isopropyl alcohol : water is 0.1-50% by weight : 30-99% by weight : 0-70% by weight.

6. The etching solution according to claim 1, wherein the weight ratio of HF : acetic acid : water is

0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

7. The etching solution according to claim 1, wherein the weight ratio of HF : tetrahydrofuran : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

8. The etching solution according to claim 1, wherein the weight ratio of HF : acetone : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

9. The etching solution according to claim 1, wherein the weight ratio of HF : methanol : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

10. The etching solution according to claim 1, wherein the weight ratio of HF : ethanol : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.

11. The etching solution according to claim 1, the solution comprising an inorganic acid.

12. The etching solution according to claim 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower.

13. The etching solution according to claim 11, wherein the weight ratio of HF : HCl : water is 0.01-50% by weight : 1-36% by weight : 0-99% by weight.

14. The etching solution according to claim 11, wherein the weight ratio of HF : HNO_3 : water is 0.01-50% by weight : 1-70% by weight : 0-99% by weight.

15. A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of claims 1-14.

16. An etched article which is obtainable by the method of claim 15.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent

In re patent application of: KEZUKA ET AL.

Serial No.: Unassigned

Examiner: Unassigned

Filed: May 22, 2001

Art Unit: Unassigned

For: ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

Atty. Docket No.:P07223US00/LRP

CHANGE OF CORRESPONDENCE ADDRESS CUSTOMER NUMBER DESIGNATION

Honorable Assistant Commissioner for Patents
Washington, D.C.
S I R:

Henceforth, please **change the correspondence address** of the above identified application to the correspondence address associated with the CUSTOMER NUMBER identified below, or to the (same) correspondence address shown below if the Customer Number designation cannot be used.

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In addition, please also **appoint the practitioners** (of LARSON & TAYLOR, PLC) associated with this Customer Number to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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Respectfully submitted,

Date: May 22, 2001

By: Douglas E. Jackson
Registration No.: 28,518

DECLARATION FOR USA PATENT APPLICATION
(including Design and National Stage PCT)

Attorney's Docket ID: P07223US00

As a below named inventor, I hereby declare that:
My residence, post office address and citizenship are as stated below adjacent to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

_____, the specification of which

_____ is attached hereto. (or)

X was filed on November 22, 1999, [ ] and was amended on _____.

[ ] as U.S. Application No. _____ (or)

[X] as International PCT Application No. PCT/JP99/06502

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) or §365 (b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, where priority is not claimed, any foreign application for patent or inventor's certificate, or any PCT International application, having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) (____ ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET):

Number	Country	Day/Month/Year Filed	Priority Not Claimed
1998-332782	Japan	24/11/1998	___
			___

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or §365(c) of any PCT International application designating the U.S., listed below; and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application. (____ ADDITIONAL APPLICATIONS IDENTIFIED ON ATTACHED SHEET.)

Application Serial No.	Day/Month/Year Filed	Status -- patented, pending, abandoned

I hereby appoint the practitioners of **LARSON AND TAYLOR** associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and direct that all correspondence be addressed to that Customer Number.

00881
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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SIGN AND DATE HERE: Inventor's Signature:	Date:

____ SEE ATTACHED SHEET FOR SIMILAR INFORMATION AND SIGNATURE FOR ADDITIONAL JOINT INVENTORS.